IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Richard W. Pekala

Confirmation No. 3559

Application No. 10/679,230

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For: **ANTIOXIDANT-COATED LEAD ACID BATTERY SEPARATORS HAVING IMPROVED ELECTRICAL AND MECHANICAL PROPERTIES**

Group Art Unit: 1771

Examiner: Hai Vo

37 C.F.R. § 1.132 DECLARATION OF RICHARD W. PEKALA

TO THE COMMISSIONER FOR PATENTS:

I, Richard W. Pekala, declare as follows:

1. I am the inventor named on the above-identified patent application.

2. I reside at 4356 NW Boxwood Drive, Corvallis, Oregon 97330.

3. In 1981, Duke University of Durham, North Carolina, awarded me a Bachelor of Science in Engineering degree. In 1983, the Massachusetts Institute of Technology (MIT) awarded me a Master of Science in Polymerics degree. The following year, MIT awarded me a Doctor of Science in Polymerics degree.

4. From 1984 to 1996, I was employed by Lawrence Livermore National Laboratory (LLNL) of Livermore, California (except for approximately nine months when I worked at Air Products and Chemicals, Inc., in Allentown, Pennsylvania). During my last six years at LLNL, I was section leader of the Polymeric Materials Group.

5. From 1996 until 1999, I was employed by PPG Industries, Inc. of Pittsburgh, Pennsylvania, where I was a scientist and Manager of the Microporous Materials Group within the Silica Products Small Business Unit.

6. From June 1999 until the present, I have been employed by Amtek Research International, LLC (the assignee of the above-identified patent application) of Lebanon, Oregon, where I am Vice-President of Research and Development.

7. I attach an English language translation of Nippon Muki Japanese Patent Application No. 1988-309711 (hereafter, Translation), which corresponds to Patent Abstract of Japan 02-155161.

8. The Translation at page 4, fifth full (last) paragraph, states that: "High-density polyethylene (weight-average molecular weight about 200,000) was used as the main component." The embodiments described in my patent application use ultrahigh molecular weight polyethylene (UHMWPE), which by definition has a molecular weight of greater than 3,100,000. The lower molecular weight of polyethylene used by Nippon Muki would make its battery separators more susceptible to oxidation. To my knowledge, no one uses or manufactures lead-acid battery separators containing only high-density polyethylene (HDPE) as the polymer matrix.

9. In the paragraphs below, I compute from the disclosure set forth in my patent application a minimum antioxidant-to-UHMWPE weight ratio of 0.17 for my battery separator and a maximum antioxidant-to-HDPE weight ratio of 0.0243 for the Nippon Muki battery separator.

10. Paragraph [0037] of my patent application states that the antioxidant coating solution is applied to the battery separator of Example 1, which begins at [0031]. Paragraph [0032] sets forth a silica-to-UHMWPE ratio of 2.5:1; and Table 1, which is part of Example 1, sets forth a 14.9% processing oil content. The battery separator of Example 1 has, therefore, a 24.3% UHMWPE ((1.00- 0.149)/3.5 = 0.243) content.

11. Table 1 sets forth a porosity of 52.7% and a density of 0.63g/cc for the battery separator of Example 1. The last sentence of [0039] sets forth a 5%-50% (w/v) range of antioxidant (Irganox 1010) dissolved in trichloroethylene (TCE). A solution containing 5% (w/v) antioxidant in TCE corresponds to 0.026g (0.05 x 0.527 = 0.026) of antioxidant for each 0.153g (0.243 x 0.63 = 0.153) of UHMWPE; therefore, the antioxidant-to-UHMWPE weight ratio is about 0.17. A solution containing 50% w/v antioxidant dissolved in TCE corresponds to 0.26g of antioxidant for each 0.153g of UHMWPE; therefore, the antioxidant-to-

UHMWPE weight ratio is about 1.71. The range of antioxidant-to-UHMWPE for the battery separator of Example 1 is between about 0.17 and about 1.71.

12. The Translation at page 3, second full paragraph, states: "It is also particularly preferred that the total amount of the antioxidant and the phosphoric acid-based peroxide decomposition agent contained in the paraffin oil be limited to no more than 5% . . .. " The Translation at page 4, fifth full (last) paragraph, states: "Each of the paraffin oils obtained was adhered to the microporous paraffin sheet samples at ratios of 10% and 20%." These two passages indicate that the Nippon Muki battery separator has no greater (and most likely less) than 1% (0.2 x 0.05 = 0.01) antioxidant distributed throughout.

13. The Translation at page 4, fifth full (last) paragraph, suggests equal amounts of high-density polyethylene and silicic acid are present in equal amounts in the battery separator, thereby giving a silica-to-polyethylene ratio of 1:1. The Translation does not specify a residual plasticizer oil content. Using the 12%-18% residual plasticizer oil content specified in [0028] of my patent application, I compute (using the same analysis presented above) for the Nippon Muki battery separator an antioxidant-to-polyethylene range of between 0.0227 and 0.0243.

14. To have an antioxidant-to-polyethylene ratio equal to the 0.17 minimum computed for the Example 1 embodiment of my battery separator, the Nippon Muki battery separator would have approximately 88% residual plasticizer oil. An 88% residual plasticizer oil would not provide a practicable, viable battery separator because there would be little, if any, available porosity.

15. The Translation at page 3, second full paragraph, states that the total amount of antioxidant and peroxide decomposition agent contained in the paraffin oil is limited to no more than 5% to prevent self-discharge. The Translation at page 4, first full paragraph, also states that the combined presence of an antioxidant and a peroxide decomposition agent not only prevents oxidation of the battery separator but also reduces softening and peeling of the active material of the positive electrode plate.

16. Having analyzed the Translation, I conclude that the Nippon Muki battery separator in comparison with the Example 1 embodiment of my battery separator uses a lower weight polyethylene (HDPE) component, constrains its maximum antioxidant content to about one-seventh the minimum of that of my battery separator, and requires a combination of

antioxidant and peroxide decomposition agent for structural robustness reasons. These demonstrate the differences in structure, composition, and operation of my separator and the Nippon Muki separator.

17. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: March 29, 2006

Richard W. Pekala

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Date examination requested	August 28, 1995
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(54) [Title of the Invention]

SEPARATOR FOR LEAD STORAGE BATTERY AND METHOD OF MANUFACTURING THE SAME

(57) [Patent Claims]

[Claim 1] A separator for a lead storage battery, in which a paraffin oil containing an antioxidant and a phosphoric acid-based peroxide decomposition agent is adhered to the inner and outer surfaces of a microporous sheet made from a synthetic resin.

[Claim 2] The separator for a lead storage battery as described in claim 1, wherein said paraffin oil contains 0.5% or more of the antioxidant and 0.5% or more of the phosphoric acid-based peroxide decomposition agent.

[Claim 3] The separator for a lead storage battery as described in claim 2, wherein the total amount of the antioxidant and the phosphoric acid-based peroxide decomposition agent contained in said paraffin oil is not more than 5%.

[Claim 4] A method of manufacturing a separator for a lead storage battery, in which an inorganic powder and an organic plasticizer are mixed with a polyolefin resin and melt molded into a sheet, all or a portion of the organic plasticizer is then extracted with an organic solvent to form a microporous sheet, and a paraffin oil containing an antioxidant and a phosphoric acid-based peroxide decomposition agent is then adhered to the inner and outer surfaces of the microporous sheet.

[Detailed Description of the Invention]

[Field of the Invention]

The present invention relates to a separator for a lead storage battery and a method of manufacturing the same.

[Prior Art]

Polyethylene separators are well known in the prior art. Such separators are manufactured by mixing a high-density polyethylene resin with an inorganic powder and organic plasticizer; melt molding into a sheet; and then obtaining a microporous structure by extracting all of the organic plasticizers, or a portion thereof, with an organic solvent. Conventional polyethylene separators are thought to have excellent resistance to oxidation.

[Problems Addressed by the Invention]

However, when such polyethylene separators are used in lead storage batteries for electric vehicles or automobiles, the utilization environment of the separators will be severe due to the increased frequency of use and high-temperature utilization conditions in recent years. Under such utilization conditions, the separator will be oxidized and degraded by the oxidation action of oxygen or lead dioxide generated from the positive alloy plate adjacent to the separator, and the intensity of this oxidation action increases with temperature. For this reason, the separator is unexpectedly rapidly oxidized and degraded, and the service life thereof is shortened, in such a severe high temperature utilization environment. On the other hand, the active material of the positive electrode plate of the lead storage battery is easily softened and peels off at such high temperatures, thereby shortening the service life of the battery.

In order to prevent the shortening of service life caused by the oxidation of the separator at high temperatures, which is the above-described drawback in the prior art, the surface of the separator is impregnated with a paraffin oil as a surface protecting agent, but such measure alone fails to provide a sufficient prevention effect with respect to the oxidation-induced degradation.

Furthermore, when an attempt was made to impregnate the separator with a paraffin oil having a phenol-based antioxidant admixed thereto, a certain amount of improvement in the prevention of oxidation-induced degradation of the separator under a high-temperature environment was observed, but the oxidation-induced degradation caused by contact with the positive electrode active material was not prevented, softening and peeling of the positive electrode active material could not be avoided, and shortening of the battery service life was impossible to avoid.

[Means to Resolve the Problems]

The present invention resolves the above-described problems, and provides a separator for a lead storage battery that has increased resistance to oxidation at high temperatures, and is comprised of a function that prevents high-temperature softening and peeling of the positive electrode active material of a lead storage battery. A paraffin oil that contains an antioxidant and a phosphorous acid-based peroxide decomposition agent is adhered to the inner and outer surfaces of a microporous sheet made from a synthetic resin.

Furthermore, the present invention provides a method of manufacturing a separator for a lead storage battery that makes it possible to reliably manufacture a separator for a lead storage battery containing both the antioxidant and the phosphoric acid-based peroxide decomposition agent of the present invention, the method characterized in that an inorganic powder and an organic plasticizer are mixed with a polyolefin resin and melt molded into a sheet, all or a portion of the organic plasticizer is then extracted with an organic solvent to form a microporous sheet, and a paraffin oil containing an

antioxidant and a phosphoric acid-based peroxide decomposition agent is then adhered to the inner and outer surfaces of the microporous sheet.

[Operation]

In the separator for a lead storage battery of the present invention, the inner surfaces of the micropores of the sheet and the outer surfaces of the sheet are covered with a paraffin oil containing an antioxidant and a phosphoric acid-based peroxide decomposition agent. Therefore, inside the battery, the oil itself will prevent the active material of the positive electrode plate, i.e., peroxide, from coming into contact with the separator sheet surfaces. At the same time, the synergetic effect of the antioxidant and phosphoric acid-based peroxide decomposition agent contained in the oil effectively prevents oxidation and chain oxidation of the separator sheet at high temperatures, and also prevents high-temperature oxidation-induced degradation and consumption of the separator sheet. In particular, it effectively prevents softening, that is, the formation of a microporous crystal structure in the positive electrode active material, i.e., lead dioxide, due to the phosphoric acid-based peroxide decomposition agent, and the peeling of the active material resulting therefrom and, therefore, greatly extends the battery service life.

In this case, it is preferred that the antioxidant contained in the paraffin oil be present at 0.5% or more based on the oil, and that the phosphoric acid-based peroxide decomposition agent be present at 0.5% or more based on the oil. It is also particularly preferred that the total amount of the antioxidant and the phosphoric acid-based peroxide decomposition agent contained in the paraffin oil be limited to no more than 5%, such limitation preventing self discharge. In order to manufacture a separator in which an oil containing relatively large amounts of the two components is reliably adhered to the inner and outer surfaces of the microporous sheet, as described in the method of manufacturing above, all or a portion of the organic plasticizer is removed with an organic solvent from a molded sheet to form a microporous sheet, and then a paraffin oil containing the prescribed amounts of the above-described components is adhered to the sheet.

[Embodiments]

An embodiment of the present invention will be described below.

The separator of the present invention is based on a microporous sheet made from a synthetic resin. However, this synthetic resin is preferably a polyolefin resin that is generally considered to have high oxidation resistance, and polyethylene, in particular high-density polyethylene, is preferred because a comparatively hard, thin and strong separator sheet can be obtained. In order to melt mold this resin and obtain a microporous sheet, for example, an inorganic powder resistant to oxidation, such as a finely powdered silicic acid, and an organic plasticizer such as ODP, are mixed at the appropriate ratios with the resin, the blend is heated and melted, and the melt is molded into a sheet by extrusion molding or the like. Then all or a portion of the plasticizer is extruded with any well-known organic solvent to produce a high-density polyethylene sheet having micropores formed therein. The present invention is characterized in that a separator for a lead storage battery is obtained in which a paraffin oil comprising an antioxidant and a phosphorus acid-based peroxide decomposition agent is adhered to the inner surfaces of the pores of the microporous sheet and the outer surfaces of the sheet. However, in the above-described manufacturing method, after the microporous sheet has been fabricated, it can be immersed for a desired amount of time in the paraffin oil containing the above-described two components, or the oil can be uniformly spread in a prescribed amount with a sprayer from the outer surfaces of the sheet, or the oil can be applied with an application roller to impregnate the microporous sheet uniformly therewith. In this case, the separator of the present invention can be manufactured by diluting the paraffin oil containing the two components at the appropriate temperature with the appropriate solvent, impregnating the microporous sheet with the oil, and then drying the solvent at a comparatively low temperature to cause the adhesion of a prescribed quantity of oil.

Furthermore, when the separator of the present invention is assembled into a lead storage battery in accordance with standard methods, the separator will be inserted between the negative electrode and

positive electrode plates to obtain an electrode assembly which is then accommodated in a battery case. As a result, a lead battery can be provided that has oxidation resistance at high temperatures and a long service life, as clearly described hereinbelow.

Note that when the above-described microporous polyethylene sheet is fabricated, in order to prevent thermal oxidation and degradation of polyethylene during heating, melting, and molding, an antioxidant is preferably added to the starting materials. However, this antioxidant is eluted in the process of extracting the plasticizer with an organic solvent, and only traces of the antioxidant are present in the microporous sheet obtained. Therefore, when the microporous sheet is used as the separator for a lead storage battery as is, surface oxidation of the sheet or chain oxidation into the inner parts thereof are unavoidably caused by lead dioxide or oxygen generated from the positive electrode plate, the sheet is oxidized and consumed, the thickness thereof decreases, and oxidation-induced degradation occurs that causes cracking in various places and formation of through holes. As a result, the internal short circuit effect occurs in the lead storage battery, and the battery becomes unsuitable for use. In particular, the oxidation-induced degradation is accelerated, and the service life of the battery is shortened, under utilization conditions such that the temperature inside the battery repeatedly increases. Accordingly, an attempt was made to prevent the separator from oxidation, by adhering a paraffin oil having an antioxidation effect to the separator, or by adhering a paraffin oil comprising only an antioxidant to the separator. As a result, a certain amount of oxidation prevention effect could be obtained. However, the active material of the positive electrode plate was softened and peeled off. Moreover, contact oxidation of the separator unavoidably occurs in this active material, thereby shortening the service life of the battery. In accordance with the present invention, as demonstrated by the results of various research, the combined presence of an antioxidant and a phosphoric acid-based peroxide decomposition agent not only prevents the oxidation of separator even when the lead storage battery is exposed to high temperatures, but also reduces softening and peeling of the active material of the positive electrode plate, thereby extending the service life of the battery, and more specifically, increases the SAE life at high temperatures.

In the present invention, any of the well-known antioxidants can be used, but phenolic antioxidants that cause no damage to the battery, such as 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), and 4,4'-thiobis(3-methyl-6-t-butylphenol), are preferred.

The peroxide decomposition agent used in accordance with the present invention has to be of the phosphoric acid type, such as TNP, because softening and peeling of the active material were found to be impossible to prevent with the peroxide decomposition agents containing no phosphoric acid, such as thiosulfide based peroxide decomposition agents.

Characteristics of the present invention will be clearly described below via comparative testing thereof.

High-density polyethylene (weight-average molecular weight about 200,000) was used as the main component. A fine powder of silicic acid and a paraffin oil as an organic plasticizer were blended at ratios of 100 wt.% and 400 wt.%, respectively, the blend was heated and melted, the mixture was molded into a sheet with a thickness of 0.5 mm with an extrusion molding apparatus, the molded sheet was passed through an organic solvent to extract all or a portion of the organic plasticizer, and then heated and dried to obtain a microporous sheet. Separately, paraffin oils were prepared that contained an antioxidant and a phosphoric acid-based peroxide decomposition agent at different blending ratios, as well as a paraffin oil containing an antioxidant and a peroxide decomposition agent containing no phosphoric acid. Each of the paraffin oils obtained was adhered to the microporous paraffin sheet samples at ratios of 10% and 20%. Furthermore, for comparison, a microporous sheet was also produced in which a paraffin oil alone was adhered to the microporous sheet.

Table 1

Separator sample No.	Content in paraffin oil			Amount of adhered oil (%)
	Antioxidant (%)	Peroxide decomposition agent		
		Based on phosphoric acid (%)	Containing no phosphoric acid (%)	

1	0.1	0.1	-	20
2A	0.5	0.5	-	10
2B	0.5	0.5	-	20
3A	1.0	1.0	-	10
3B	1.0	1.0	-	20
4A	1.0	4.0	-	10
4B	1.0	4.0	-	20
5	2.0	1.0	-	20
6	3.0	1.0	-	20
7	4.0	1.0	-	20
8	5.0	-	-	20
9	-	4.0	-	20
10	-	-	4.0	20
11	1.0	-	4.0	20
12	-	-	-	-

Lead storage batteries for automobiles were prepared by using the separators for lead storage batteries of the above-described samples No. 1 to No. 12, and assembling electrode assemblies by laminating the separators with negative electrode plates and positive electrode plates for lead storage batteries. Then, the tests were conducted to determine the 5-h ratio capacity, C.C.A., overcharge life, and 65° SAE life of the test battery samples No. 1' to No. 12' corresponding to respective separators. The measurement results are shown in Table 2. .

Table 2

Lead storage battery sample No.	5-h ratio capacity (Ah)	C.C.A. (A)	Overcharge life (cycles)	65°C SAE life (cycles)
1'	28.5	293	4	2500
2'A	28.5	294	6	2900
2'B	28.5	293	6	3000
3'A	28.5	292	8	3250
3'B	28.3	295	8	3500
4'A	28.3	290	8	3300
4'B	28.5	295	8	3400
5'	28.5	295	6	2950
6'	28.5	294	6	2900
7'	28.5	294	6	2900
8'	28.4	293	5	2550
9'	28.4	294	5	3000
10'	28.5	294	5	2500
11'	28.5	294	6	2500
12'	28.5	294	4	2400

Data shown in Table 1 and Table 2 demonstrate that the test batteries No. 2A' to No. 7' using the separators No. 2A to No. 7 in accordance with the present invention, in which the antioxidant and phosphorus acid-based peroxide decomposition agent were adhered to the separators, demonstrated a significant extension of both the overcharge life and 65°C SAE life in comparison to the batteries using the conventional separators No. 1' and No. 12'. Furthermore, in the battery No. 8 using the separator No. 8 in which an oil comprising only the antioxidant was adhered thereto (comparative test), as shown in Table 2, an extension of the service life of the two types was not observed. Furthermore, in the battery No. 8' using the separator No. 9 in which an oil comprising only the phosphoric acid-based peroxide decomposition agent was adhered thereto, as shown in the same table,

an improvement in SAE life was observed, but practically no extension of overcharge life was observed. Moreover, when the battery was disassembled upon completion of the test and the separator thereof was inspected, the separator was found to have undergone oxidation-induced degradation, the thickness of the sheet decreased, and cracks appeared in various places therein. Furthermore, as shown in the same table, absolutely no extension of SAE life was observed in a battery 11', which respectively used a separator No. 10, to which an oil containing only a peroxide decomposition agent containing no phosphoric acid was adhered, in order to study the effects thereof, and a separator No. 11 to which an oil containing this and an antioxidant was adhered, in order to study the combined effects thereof. Moreover, the oxidation-induced degradation of the separators in the batteries No. 10, No. 10', and No. 11' was found to be similar to that of the sample No. 8 (No. 8').

With respect to all the separator samples and test batteries, softening and peeling of the active material was inspected for the positive electrode plates that came into contact with the separators (the results are not shown in the tables). In all the batteries using the conventional separators No. 1 and No. 12 and also the comparative separators No. 8 to No. 11, softening and peeling were observed. By contrast, in the batteries using the separators No. 2 to No. 7 in accordance with the present invention, in which both the antioxidant and the phosphoric acid-based peroxide decomposition agent were adhered thereto, absolutely no oxidation-induced degradation of the separator was observed, and absolutely no softening and peeling of the active material of the positive electrode plate that is in contact therewith was observed. In particular, when an oil containing both components was adhered to the separator sheet, as in samples No. 3A, 3B, 4A, and 4B, an excellent service life extension effect providing an overcharge life of 8 cycles and a SAE life of 3000 or more was observed.

[Effect of the Invention]

The separator in accordance with the present invention comprises a microporous sheet made from a synthetic resin and having adhered thereto a paraffin oil comprising an antioxidant and a phosphoric acid-based peroxide decomposition agent. Therefore, when this separator is used in a lead storage battery, there will be no oxidation-induced degradation of the separator even when the battery is used at high temperatures. Furthermore, softening and peeling of the positive electrode active material of the positive electrode plate that is in contact with the separator is prevented, and a significant extension of the charge-discharge cycle life of the lead storage battery at high temperatures is attained. Moreover, when the separator of the present invention is manufactured, the paraffin oil containing an antioxidant will be adhered after the microporous sheet has been manufactured. Therefore, the desired amount of antioxidant and phosphoric acid-based peroxide decomposition agent can be reliably adhered to the inner and outer surface of the separator.